

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

**0 381 216
A1**

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 90102015.6

(51) Int. Cl.⁵: **C11D 7/50, C23G 5/028,
C07C 19/08**

(22) Date of filing: **01.02.90**

Additional priorities: 150889 JP 20968489;
120989 JP 23460289, 23460389, 23460489,
23460589; 061089 JP 26016489 and 26016589.

(30) Priority: 01.02.89 JP 20883/89

01.02.89 JP 20887/89

01.02.89 JP 20888/89

02.02.89 JP 22532/89

02.02.89 JP 22539/89

02.02.89 JP 22549/89

06.02.89 JP 25642/89

06.02.89 JP 25643/89

06.02.89 JP 25686/89

06.02.89 JP 25687/89

06.02.89 JP 25688/89

14.02.89 JP 32834/89

26.04.89 JP 104650/89

26.04.89 JP 104651/89

26.05.89 JP 131531/89

30.05.89 JP 134606/89

30.05.89 JP 134607/89

30.06.89 JP 167107/89

14.08.89 JP 207842/89

14.08.89 JP 207843/89

(4) Date of publication of application:
08.08.90 Bulletin 90/32

(54) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IT LI LU NL SE

(71) Applicant: **ASAHI GLASS COMPANY LTD.**

1-2, Marunouchi 2-chome

Chiyoda-ku Tokyo 100(JP)

(72) Inventor: Samejima, Shunichi

2-49-15, Chuo, Nakano-ku

Tokyo(JP)

Inventor: Kitamura, Kenroh

2-7-24, Sakuragaoka, Kugenuma

Fujisawa-shi, Kanagawa-ken(JP)

Inventor: Watanabe, Naohiro

1-26-2, Tsuganodai

Chiba-shi, Chiba-ken(JP)

Inventor: Asano, Teruo

543, Sanmai-cho, Kanagawa-ku

Yokohama-shi, Kanagawa-ken(JP)

Inventor: Kamimura, Toru

5232-2, Goi, Ichihara-shi

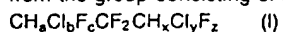
Chiba-ken(JP)

EP 0 381 216 A1

74 Representative: Wächtershäuser, Günter, Dr.
Tal 29
D-8000 München 2(DE)

54 Hydrochlorofluorocarbon azeotropic or azeotropic-like mixture.

57 A hydrochlorofluorocarbon azeotropic or azeotropic-like mixture comprising at least one member selected from the group consisting of hydrogen-containing fluoropropanes of the formula I:



wherein $a+b+c=3$, $x+y+z=3$, $a+x \geq 1$, $b+y \geq 1$, and $0 \leq a, b, c, x, y, z \leq 3$, and at least one member selected from the group of compounds II consisting of halogenated hydrocarbons having a boiling point of from 20 to 85°C other than said hydrochlorofluoropropanes, hydrocarbons having a boiling point of from 20 to 85°C and alcohols having from 1 to 4 carbon atoms.

HYDROCHLOROFLUOROCARBON AZEOTROPIC OR AZEOTROPIC-LIKE MIXTURE

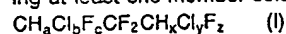
The present invention relates to a novel hydrochlorofluorocarbon azeotropic or azeotropic-like mixture which can be used as a chlorofluorocarbon alternative and which has excellent properties as a solvent and so on.

Chlorofluorocarbon compounds (hereinafter referred simply as CFCs) have little toxicity and are, in many cases, non-flammable and chemically stable. Various CFCs having different boiling points are available. By virtue of such properties, 1,1,2-trichloro-1,2,2-trifluoroethane (R113) is used as a solvent or a blowing agent; trichloromonofluoromethane (R11) is used as a blowing agent or a propellant; and dichlorodifluoromethane (R12) is used as a propellant or a refrigerant.

Chemically stable R11, R12 and R113 have long lifetime in the troposphere and reach the stratosphere, where they will be dissociated by solar radiation to release chlorine radicals, which initiate a chain reaction with ozone and deplete the ozone layer. Accordingly, the regulations for limiting the use of such conventional CFCs have been implemented. Therefore, a research has been actively conducted to develop a CFC alternative which scarcely depletes the ozone layer.

It is an object of the present invention to provide a mixture containing a novel hydrochlorofluoropropane having 3 carbon atoms, which has various excellent properties equal to conventional CFCs and which is useful as a CFC alternative.

The present invention provides a hydrochlorofluorocarbon azeotropic or azeotropic-like mixture comprising at least one member selected from the group consisting of hydrochlorofluoropropanes of the formula I:



wherein $a+b+c=3$, $x+y+z=3$, $a+x \geq 1$, $b+y \geq 1$, and $0 \leq a, b, c, x, y, z \leq 3$, and at least one member selected from the group of compounds II consisting of halogenated hydrocarbons having a boiling point of from 20 to 85°C other than the above hydrochlorofluoropropanes, hydrocarbons having a boiling point of from 20 to 85°C and alcohols having from 1 to 4 carbon atoms.

The mixture of the present invention is non-flammable or hardly flammable and may take a form of an azeotropic composition or an azeotropic-like composition. Particularly when used as a solvent, it provides properties equal or superior to conventional 1,1,2-trichlorotrifluoroethane (R113). Therefore, it is very useful as an alternative for R113. Further, no substantial change in the composition was observed when boiling or evaporating. Therefore, it may be used in the same manner as a conventional single CFC, whereby it has a merit in that no substantial change in the conventional technique is required.

The hydrochlorofluoropropanes of the formula I in the present invention contain a hydrogen atom and a fluorine atom as essential elements and may further contain a chlorine atom. Specifically, they include the following compounds:

CClF₂CF₂CHCl₂ (R224ca)
 CCl₂FCF₂CHClF (R224cb)
 CF₃CF₂CHCl₂ (R225ca)
 CClF₂CF₂CHClF (R225cb)
 CClF₂CF₂CH₂Cl (R234cc)
 CHF₂CF₂CHClF (R235ca)
 CH₃CF₂CCl₂F (R243cc)
 CHF₂CF₂CH₂Cl (R244ca)
 CH₂ClCF₂CH₂Cl (R252ca)
 CHCl₂CF₂CH₃ (R252cb)
 CH₃CF₂CH₂Cl (R262ca)
 CHF₂CF₂CClF (R225cc)
 CHClFCF₂CHClF (R234ca)
 CHF₂CF₂CHCl₂ (R234cb)
 CH₂FCF₂CCl₂F (R234cd)
 CF₃CF₂CH₂Cl (R235cb)
 CClF₂CF₂CH₂F (R235cc)
 CH₂ClCF₂CHClF (R243ca)
 CH₂FCF₂CHCl₂ (R243cb)
 CH₂FCF₂CHClF (R244cb)
 CClF₂CF₂CH₃ (R244cc)
 CH₂FCF₂CH₂Cl (R253ca)
 CH₃CF₂CHClF (R253cb)

$\text{CF}_3\text{CF}_2\text{CHClF}$ (R226ca)
 $\text{CClF}_2\text{CF}_2\text{CHF}_2$ (R226cb)
 $\text{CCl}_3\text{CF}_2\text{CHCl}_2$ (R222c)
 $\text{CCl}_2\text{FCF}_2\text{CHCl}_2$ (R223ca)
5 $\text{CCl}_3\text{CF}_2\text{CHClF}$ (R223cb)
 $\text{CCl}_3\text{CF}_2\text{CHF}_2$ (R224cc)
 $\text{CHCl}_2\text{CF}_2\text{CHCl}_2$ (R232ca)
 $\text{CCl}_3\text{CF}_2\text{CH}_2\text{Cl}$ (R232cb)
 $\text{CCl}_2\text{FCF}_2\text{CH}_2\text{Cl}$ (R233cb)
10 $\text{CHCl}_2\text{CF}_2\text{CHClF}$ (R233ca)
 $\text{CCl}_3\text{CF}_2\text{CH}_2\text{F}$ (R233cc)
 $\text{CCl}_3\text{CF}_2\text{CH}_3$ (R242cb)
 $\text{CHCl}_2\text{CF}_2\text{CH}_2\text{Cl}$ (R242ca)

Among them, preferred are R225ca, R225cb, R244ca, R244cb, R235ca and R243cc.

15 The halogenated hydrocarbons having a boiling point of from 20 to 85° C other than the hydrochlorofluoropropanes of the formula I, include chlorinated hydrocarbons, fluorinated hydrocarbons and brominated hydrocarbons having from 1 to 4 carbon atoms.

The chlorinated hydrocarbons having from 1 to 4 carbon atoms, include dichloromethane, trichloromethane, trans-1,2-dichloroethylene, cis-1,2-dichloroethylene, 1-chloropropane, 2-chloro-2-methylpropane, 1,1,1-trichloroethane and 1,1-dichloroethane. The fluorinated hydrocarbons include 1,1,2-trichlorotrifluoroethane (R113), 1,1,2-trichloro-2,2-difluoroethane (R122), 1,2,2-trichloro-1,2-difluoroethane (R122a), 1,1,1-trichloro-2,2-difluoroethane (R122b), 1,1-dichloro-2,2,2-trifluoroethane (R123), 1,2-dichloro-1,1-difluoroethane (R132b), 1,2-dichloro-1-fluoroethane (R141), 1,1-dichloro-1-fluoroethane (R141b) and trichlorofluoromethane (R11). Likewise, the brominated hydrocarbons include 2-bromopropane as a preferred

25 example.
 The hydrocarbons having a boiling point of from 20 to 85° C, include aliphatic, alicyclic and aromatic hydrocarbons. Preferably, they include hydrocarbons having from 5 to 8 carbon atoms such as n-pentane, isopentane, n-hexane, 2,4-dimethylpentane, cyclopentane, 2,2-dimethylbutane, 2-methylpentane, methylcyclopentane, cyclohexane and 2,3-dimethylbutane. The hydrocarbons having from 5 to 8 carbon atoms

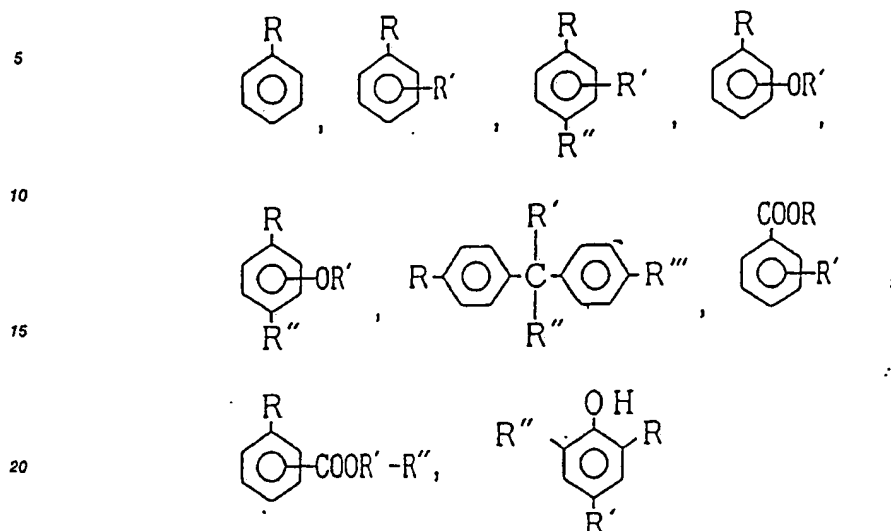
30 may be a mixture obtained as a petroleum fraction and may preferably be a petroleum fraction containing as the main component at least one member selected from the group consisting of cyclopentane, 2,2-dimethylbutane, 2-methylpentane and 2,3-dimethylbutane.

The azeotropic or azeotropic-like composition of the mixture of the present invention may vary to an extent of $\pm 1.0\%$ by weight depending upon the purities of the compounds to be mixed or by the influence
 35 of measuring error, etc.
 To the mixture of the present invention, other components may further be incorporated, as the case requires. For example, when the mixture is used as a solvent, it may contain at least one member selected from the group consisting of hydrocarbons such as neopentane, 3-methylpentane, neohexane, hexane, 3-methylhexane, heptane, isoheptane, 2,3-dimethylpentane, 2,4-dimethylpentane, octane, 2,2,3-trimethylpentane, 2,2,4-trimethylpentane, cyclopentane, methylcyclohexane and ethylcyclohexane; chlorinated hydrocarbons
 40 such as 1,1,2-trichloroethane, 1,2-dichloroethane, trichloroethylene and tetrachloroethylene; chlorofluorinated hydrocarbons other than those of the present invention, such as 1,1-dichloro-2,3,3,3-tetrafluoropropene-1, trans-3-chloro-1,1,1,2,4,4,5,5,5-nonafluoropentene-2, cis-3-chloro-1,1,1,2,4,4,5,5,5-nonafluoropentene-2, 1,1,1,2,2,5,5,6,6,6-decafluorohexane and tetrachloro-1,2-difluoroethane; nitro compounds;
 45 phenols; amines; ethers; amlenes; esters; organic phosphites; epoxides; furans; alcohols; ketones; amides; and triazoles.

The content of such additional components in the mixture of the present invention is not particularly limited, but for the purpose of improving or controlling the solubility or obtaining a suitable boiling point or non-flammability, the content is usually from 0 to 50% by weight, preferably from 1 to 40% by weight.
 50 Preferably such incorporation will bring about an azeotropic or azeotropic-like composition. Further, to give the mixture a high level of stabilizing effect, it is effective to incorporate a stabilizer. The content of such additional components is usually from 1 ppm to 10% by weight, preferably from 10 ppm to 5% by weight. Further, the mixture of the present invention may further contain various cleaning assistants, surfactants, emulsifying agents, water, etc.

55 As the nitro compounds, those represented by the formula R-NO_2 wherein R is a chain or cyclic hydrocarbon group having from 1 to 6 carbon atoms and containing a saturated or unsaturated bond, may be employed. Specifically, they include nitromethane, nitroethane, 1-nitropropane, 2-nitropropane and nitrobenzene. More preferred are nitromethane and nitroethane.

As the phenols, those represented by the following formulas are preferred:



25 wherein each of R, R', R'' and R''' is OH or a chain or cyclic hydrocarbon group having from 1 to 6 carbon atoms and containing a saturated or unsaturated bond.

Specifically, they include phenol, o-cresol, m-cresol, p-cresol, thymol, p-tert-butylphenol, tert-butylcatechol, catechol, isoeugenol, o-methoxyphenol, 4,4'-dihydroxyphenyl-2,2-propane, isoamyl salicylate, benzyl salicylate, methyl salicylate and 2,6-di-t-butyl-p-cresol. More preferred are phenol, 4,4-dihydroxyphenyl-2,2-propane and 2,6-di-t-butyl-p-cresol.

30 As the amines, those represented by the following formulas are preferred:

R-N(R')₂, (R)₂-N(R')₂, (R)₂-NR', (R)₃N, RN,



(R)₂N-R'-N-(R'')

R-CHN(R')₂-R''-N-(R'')

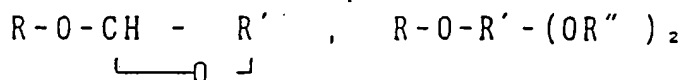
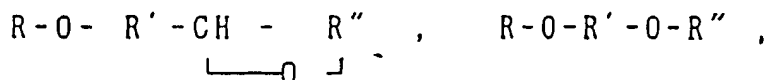
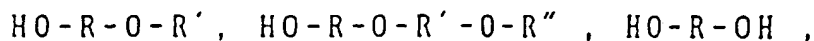
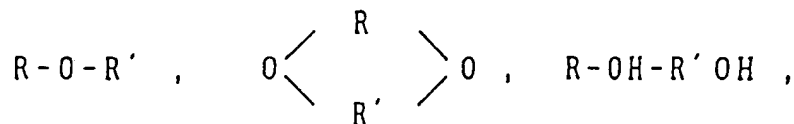
(R)₂N-R'-NH-R''-N-(R'')

(R)₂N-(R'NH)₄-R'', R-NH-R', and (R)₂-N-OR'

45 wherein each of R, R', R'' and R''' is a hydrogen atom or a chain or cyclic hydrocarbon group having from 1 to 8 carbon atoms and containing a saturated or unsaturated bond.

Specifically, they include pentylamine, hexylamine, diisopropylamine, diisobutylamine, di-n-propylamine, diallylamine, triethylamine, n-methylaniline, pyridine, picoline, morpholine, N-methylmorpholine, triallylamine, allylamine, α-methylbenzylamine, methylamine, dimethylamine, trimethylamine, ethylamine, diethylamine, propylamine, isopropylamine, sec-butylamine, tert-butylamine, dibutylamine, tributylamine, dipentylamine, tripentylamine, 2-ethylhexylamine, aniline, N,N-dimethylaniline, N,N-diethylaniline, ethylenediamine, propylenediamine, diethylenetriamine, tetraethylenepentamine, benzylamine, dibenzylamine, diphenylamine and diethylhydroxylamine. More preferred are diisopropylamine and diallylamine.

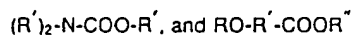
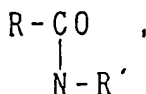
55 As the ethers, those represented by the following formulas are preferred:



wherein each of R, R' and R'' is a chain or cyclic hydrocarbon group having from 1 to 10 carbon atoms and containing a saturated or unsaturated bond. Specifically, they include 1,4-dioxane, 1,2-butanediol, isopropyl ether, ethylene glycol monomethyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, dipropylene glycol methyl ether, ethyl isobutyl ether, ethyl isopentyl ether, ethyl naphthyl ether, ethyl vinyl ether, ethyl phenyl ether, anisole, anethole, ethyl propargyl ether, ethyl propyl ether, ethyl methyl ether, ethylene glycol, methyl glycidyl ether, ethylene glycol diethyl ether, ethylene glycol diphenyl ether, ethylene glycol dimethyl ether, ethylene glycol monophenyl ether, ethylene glycol monobutyl ether, ethylene glycol monobenzyl ether, dipentyl ether, allyl ethyl ether, diisopentyl ether, diallyl ether, butyl glycidyl ether, allyl glycidyl ether, dipropyl ether, ethyl glycidyl ether, vinyl glycidyl ether, dimethyl ether, diethyl ether, di-n-propyl ether, dibutyl ether, 1,2-dimethoxyethane, trimethoxyethane, and triethoxyethane. More preferred are 1,4-dioxane, butyl glycidyl ether and 1,2-dimethoxyethane.

As the amylenes, α -amylenes, β -amylenes, γ -amylenes, α -isoamylenes and β -isoamylenes are preferred. More preferred is β -amylenes.

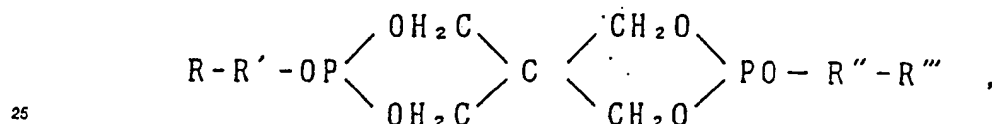
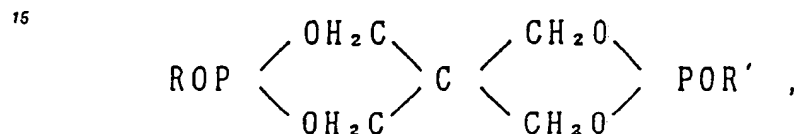
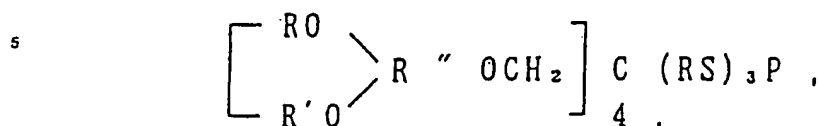
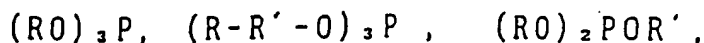
As the esters, those represented by the following formulas are preferred:
 $R-COO-R'$



wherein each of R, R' and R'' is a hydrogen atom or a chain or cyclic hydrocarbon group having from 1 to 6 carbon atoms and containing a saturated or unsaturated bond.

Specifically, they include methyl acetate, ethyl acetate, propyl acetate, n-butyl acetate, isobutyl acetate, isopropyl acetate, ethyl acrylate, 2-hydroxyethyl methacrylate, methyl acrylate, butyl acrylate, phenyl acrylate, allyl acrylate, caprolactam, ethyl carbamate, methyl carbamate, and methyl salicylate. More preferred are methyl acetate and methyl salicylate.

As the organic phosphites, those represented by the following formula are preferred:



wherein each of R, R', R'' and R''' is a hydrogen atom or a saturated or unsaturated chain or cyclic hydrocarbon group having from 1 to 18 carbon atoms. Specifically, they include triphenylphosphite, tris(nonylphenyl)phosphite, triethylphosphite, tris(2-ethylhexyl)phosphite, tridecylphosphite, tributylphosphite, diphenylmono(2-ethylhexyl)phosphite, diphenylmonodecylphosphite, diphenylmonotridecylphosphite, dilaurylhydrogen phosphite, diphenylhydrogen phosphite, tetraphenyldipropylene glycol pentaerythritol tetraphosphite, trilauryltrithiophosphite, bis(tridecyl)pentaerythritol diphosphite, bis(nonylphenyl)pentaerythritol diphosphite, tristearyl phosphite, distearyl pentaerythritol diphosphite, and tris(2,4-di-tert-butylphenyl)phosphite. More preferred are triphenylphosphite and tributylphosphite.

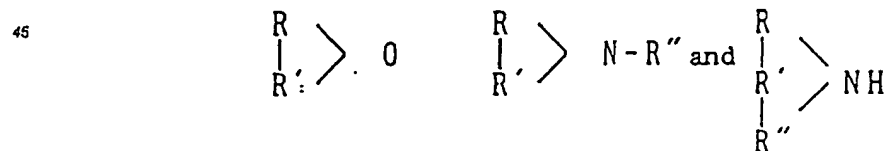
As the epoxides, those represented by the following formulas are preferred:

RO and XRO

wherein R is a saturated or unsaturated chain or cyclic hydrocarbon group having from 1 to 8 carbon atoms, and X is a halogen atom.

Specifically, they include 1,2-butylene oxide, epichlorohydrin, propylene oxide, 2,3-butylene oxide and styrene oxide. More preferred are 1,2-butylene oxide and epichlorohydrin.

As the furans, those represented by the following formulas are preferred:



wherein each of R, R' and R'' is a saturated or unsaturated hydrocarbon group having from 1 to 2 carbon atoms. Specifically they include tetrahydrofuran, n-methylpyrrole, 2-methylpyrrole and 3-methylpyrrole. More preferred is N-methylpyrrole.

As the alcohols which are mainly used as stabilizers, those presented by the following formulas are preferred:

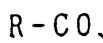
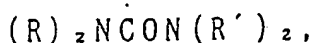
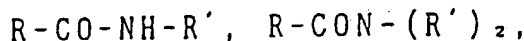
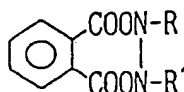
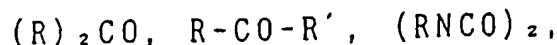
R-OH, NH₂-R-OH, R-O-R'-OH and R-R'-OH

wherein each of R and R' is a saturated or unsaturated chain or cyclic hydrocarbon group having from 1 to

6 carbon atoms.

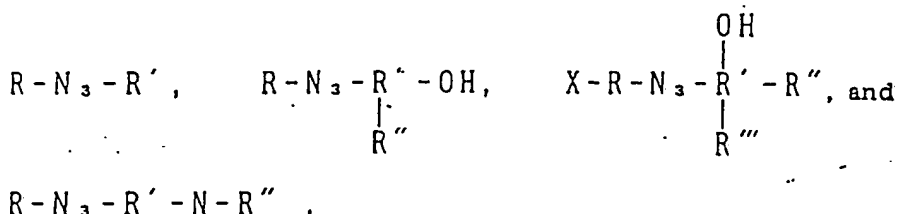
Specifically, they include, methanol, ethanol, secbutanol, tert-butanol, allyl alcohol, benzyl alcohol, propanol, isopropanol, tert-amyl alcohol, 1-amino-2-propanol, propargyl alcohol, isobutanol, butanol, 3-methylpentyn-3-ol, 1-methoxy-2-propanol, 3-methyl-1-butyne-3-ol, 2-methyl-3-butyne-3-ol, pentyl alcohol, hexanol, heptanol and octanol. More preferred are secbutanol and propargyl alcohol.

As the ketones and amides, those represented by the following formulas are preferred:



wherein each of R, R', R'' and R''' is a hydrogen atom or a saturated or unsaturated hydrocarbon group having from 1 to 4 carbon atoms. Specifically, they include acetone, methyl ethyl ketone, methyl isobutyl ketone, azodicarbonamide, maleic acid hydrazine, phthalic acid hydrazine, formamide, N-methylformamide, N,N-dimethylformamide, N-methylpropionamide, 2-pyrrolidone, N,N,N'-tetramethylurea and N-methylpyrrolidone. More preferred are methyl isobutyl ketone and 2-pyrrolidone.

As the triazoles, those presented by the following formulas are preferred:



wherein each of R, R', R'' and R''' is a hydrogen atom or a saturated or unsaturated chain or cyclic hydrocarbon group having from 1 to 16 carbon atoms, and X is a halogen atom.

Specifically, they include 2-(2'-hydroxy-5'-methylphenyl)benzotriazole, 2-(2'-hydroxy-3'-tert-butyl-5'-methylphenyl)-5-chlorobenzotriazole, 1,2,3-benzotriazole, and 1-[(N,N-bis-2-ethylhexyl)aminomethyl]-benzotriazole. More preferred is 1,2,3-benzotriazole.

The hydrochlorofluorocarbon azeotropic or azeotropic-like mixture of the present invention is useful for various purposes, for example, as a blowing agent and so on, like conventional CFCs. It is particularly useful as a solvent, since it provides a solvency equivalent or superior to conventional R113. Specific applications as the solvent include a removing agent for flux, grease, oil, wax or ink, a coating solvent, an extracting agent, a cleaning or water-removing agent for various articles made of glass, ceramics, plastic, rubber or metal, particularly for semiconductor devices, electronic components, electronic circuit boards, electrical devices, precision machine parts or optical lenses. Further, it is useful as a resist developer, a resist-removing agent or a buff polishing and cleaning agent. As a cleaning method, manual wiping, dipping, spraying, shaking, ultrasonic cleaning or vapor cleaning may be employed.

Now, the present invention will be described in further detail with reference to Examples. However, it should be understood that the present invention is by no means restricted by such specific Examples.

5 EXAMPLES 1 to 152

1,000 g of a mixture as identified in Table 1 was charged in a distillation flask, and using a packed distillation column which contained approximately 20 theoretical plates, distillation was conducted under atmospheric pressure. The fractions thereby obtained were measured by gas chromatography, whereby the
10 presence of an azeotropic composition was found.

On the other hand, the azeotropic-like composition was obtained from the composition after repeating the evaporation and condensation of a mixture as identified in Table 1 for 3 days by an open system cleaning sump.

A SUS-304 test piece (25 mm x 30 mm x 2 mm in thickness) was immersed in machine oil (CQ-30, manufactured by Nippon Sekiyu K.K.) and then immersed in the azeotropic mixture of the present invention for 5 minutes. The results are shown in Table 1, wherein symbol A-⊙ indicates that the machine oil can be removed satisfactorily at the same level as R113.
15

A single sided printed circuit board (50 mm x 100 mm x 1.6 mm in thickness) was coated with a flux (Tamura F-AL-4, manufactured by Tamura Seisakusho) and heated at 200 °C for 2 minutes in a convection oven. Then, it was immersed in the azeotropic mixture of the present invention for one minute. The results are shown in Table 1, in which symbol B-⊙ indicates that the flux can be removed satisfactorily at the same level as R113/ethanol = 96.2 wt%/3.8 wt%.
20

A glass plate (30 mm x 18 mm x 5 mm in thickness) was immersed in deionized water and then immersed in the azeotropic mixture of the present invention for 20 seconds for removal of water. The glass plate withdrawn, was immersed in dry methanol, whereby the removal of water was determined from the increase of the water content in methanol. The results are shown in Table 1, in which symbol C-⊙ indicates that the water can be removed satisfactorily at the same level as R113/methanol = 93.6 wt%/6.4 wt%.
25

30

35

40

45

50

55

Table 1

Exam- ples	Mixtures	B.P. (°C)	Charged composi- tion (wt%)	Boiling point of Azeo- trope (°C)	Azeo- tropic compo- sition (wt%)	Azeo- tropic- like compo- sition (wt%)	Test results
1	R225ca R141b	51.1 32	30 70	31	25 75	5-45 55-95	A-⊙
2	R225ca R113	51.1 47.6	40 60	44	42 58	22-62 38-78	A-⊙
3	R225ca R122	51.1 71.9	80 20	52	78 22	58-98 2-42	A-⊙
4	R225ca R132b	51.1 46.8	52 48	42	50 50	30-70 30-70	A-⊙
5	R225ca Dichloro- methane	51.1 39.8	50 50	34	47 53	27-67 33-73	B-⊙
6	R225cb R141b	56.1 32	20 80	32	16 84	1-36 64-99	A-⊙
7	R225cb Dichloro- methane	56.1 39.8	50 50	36	43 57	33-53 47-67	B-⊙
8	R225cb R132b	56.1 46.8	42 58	43	39 61	19-59 41-81	A-⊙
9	R225cb R122	56.1 71.9	80 20	55	78 22	58-98 2-42	A-⊙
10	R225cb R113	56.1 47.6	30 70	46	32 68	12-52 48-88	A-⊙
11	R244ca R141b	54 32	15 85	32	13 87	1-33 67-99	A-⊙
12	R244ca Dichloro- methane	54 39.8	50 50	35	38 62	18-58 42-82	A-⊙ B-⊙

Table 1 (continued)

Exam- ples	Mixtures	B.P. (°C)	Charged composi- tion (wt%)	Boiling point of Azeo- trope (°C)	Azeo- tropic compo- sition (wt%)	Azeo- tropic- like compo- sition (wt%)	Test results
13	R244ca R122	54 71.9	80 20	55	83 17	63-99 1-37	A-⊙
14	R244ca R132b	54 46.8	42 58	44	38 62	18-58 42-82	A-⊙
15	R244ca R113	54 47.6	20 80	47	26 74	6-46 54-94	A-⊙
16	R225ca Cyclo- pentane	51.1 49.3	70 30	45	66 34	46-98 2-54	A-⊙
17	R225cb Cyclo- pentane	56.1 49.3	58 42	47	55 45	35-98 2-65	A-⊙
18	R244ca 2,2- dimethyl- butane	54 49.7	50 50	50	48 52	28-98 2-72	A-⊙
19	R225cb 2,2- dimethyl- butane	56.1 49.7	25 75	50	21 79	11-98 2-89	A-⊙
20	R244ca Cyclo- pentane	54 49.3	55 45	47	50 50	30-98 2-70	A-⊙
21	R225ca 2,2- dimethyl- butane	51.1 49.7	60 40	49	56 44	36-98 2-64	A-⊙

Table 1 (continued)

Examp- ples	Mixtures	B.P. (°C)	Charged composi- tion (wt%)	Boiling point of Azeo- trope (°C)	Azeo- tropic compo- sition (wt%)	Azeo- tropic- like compo- sition (wt%)	Test results
22	R225ca 2-bromo- propane	51.1 59.4	60 40	47	66 34	46-86 14-54	A-⊙
23	R225cb 2-bromo- propane	56.1 59.4	60 40	49	58 42	38-78 22-62	A-⊙
24	R244ca 2-bromo- propane	54 59.4	50 50	48	55 45	35-75 25-65	A-⊙
25	R244cb 2-bromo- propane	58 59.4	60 40	50	50 50	30-70 30-70	A-⊙
26	R235ca 2-bromo- propane	43.9 59.4	70 30	42	74 26	54-94 6-46	A-⊙
27	R243cc 2-bromo- propane	60.2 59.4	40 60	52	50 50	30-70 30-70	A-⊙
28	R225cb 2-methyl- pentane	56.1 60.3	90 10	-	- -	50-99 1-50	A-⊙
29	R244ca 2-methyl- pentane	54 60.3	90 10	55	91 9	71-99 1-29	A-⊙
30	R244cb 2-methyl- pentane	58 60.3	70 30	55	72 28	52-98 2-48	A-⊙

Table 1 (continued)

Exam- ples	Mixtures	B.P. (°C)	Charged composi- tion (wt%)	Boiling point of Azeo- trope (°C)	Azeo- tropic compo- sition (wt%)	Azeo- tropic- like compo- sition (wt%)	Test results
31	R243cc 2-methyl- pentane	60.2 60.3	70 30	61	74 26	54-99 1-46	A-⊙
32	R225cb 2,3- dimethyl- butane	56.1 58.0	80 20	56	78 22	58-98 2-42	A-⊙
33	R244ca 2,3- dimethyl- butane	54 58.0	80 20	53	76 24	56-96 4-44	A-⊙
34	R244cb 2,3- dimethyl- butane	58 58.0	60 40	55	63 37	43-95 5-57	A-⊙
35	R225ca 2,3- dimethyl- butane	51.1 58.0	90 10	-	- -	85-99 1-15	A-⊙
36	R243cc 2,3- dimethyl- butane	60.2 58.0	90 10	-	- -	50-95 5-50	A-⊙
37	R225ca trans- 1,2- dichloro- ethylene	51.1 47.7	60 40	44	57 43	37-77 23-63	A-⊙

Table 1 (continued)

Exam- ples	Mixtures	B.P. (°C)	Charged composi- tion (wt%)	Boiling point of Azeo- trope (°C)	Azeo- tropic compo- sition (wt%)	Azeo- tropic- like compo- sition (wt%)	Test results
38	R225cb trans- 1,2- dichloro- ethylene	56.1 47.7	50 50	46	47 53	27-67 33-73	A-⊙
39	R244ca trans- 1,2- dichloro- ethylene	54 47.7	50 50	45	46 54	27-66 34-74	A-⊙
40	R244cb trans- 1,2- dichloro- ethylene	58 47.7	45 55	46	40 60	20-60 40-80	A-⊙
41	R235ca trans- 1,2- dichloro- ethylene	43.9 47.7	70 30	41	66 34	46-86 14-54	A-⊙
42	R243cc trans- 1,2- dichloro- ethylene	60.2 47.7	40 60	45	42 58	22-62 38-78	A-⊙
43	R225ca cis-1,2- dichloro- ethylene	51.1 60.6	80 20	50	78 22	58-98 2-42	A-⊙

Table 1 (continued)

Exam- ples	Mixtures	B.P. (°C)	Charged composi- tion (wt%)	Boiling point of Azeo- trope (°C)	Azeo- tropic compo- sition (wt%)	Azeo- tropic- like compo- sition (wt%)	Test results
44	R225cb cis-1,2- dichloro- ethylene	56.1 60.6	70 30	53	69 31	59-79 21-41	A-⊙
45	R244ca cis-1,2- dichloro- ethylene	54 60.6	70 30	51	67 33	47-87 13-53	A-⊙
46	R244cb cis-1,2- dichloro- ethylene	58 60.6	60 40	54	59 41	39-79 21-61	A-⊙
47	R235ca cis-1,2- dichloro- ethylene	43.9 60.6	90 10	45	94 6	74-99 1-26	A-⊙
48	R243cc cis-1,2- dichloro- ethylene	60.2 60.6	60 40	52	58 42	38-78 22-62	A-⊙
49	R244cb R113	58 47.6	10 90	48	12 88	2-32 68-98	A-⊙
50	R235ca R113	43.9 47.6	60 40	42	56 44	36-76 24-64	A-⊙
51	R244cb Dichloro- methane	58 39.8	30 70	36	33 67	13-53 47-87	A-⊙
52	R235ca Dichloro- methane	43.9 39.8	50 50	32	53 47	33-73 27-67	A-⊙

Table 1 (continued)

Exam- ples	Mixtures	B.P. (°C)	Charged composi- tion (wt%)	Boiling point of Azeo- trope (°C)	Azeo- tropic compo- sition (wt%)	Azeo- tropic- like compo- sition (wt%)	Test results
53	R243cc Dichloro- methane	60.2 39.8	50 50	38	30 70	10-50 50-90	A-⊙
54	R244cb Cyclo- pentane	58 49.3	40 60	48	43 57	23-99 1-77	A-⊙
55	R235ca Cyclo- pentane	43.9 49.3	80 20	42	77 23	67-99 1-33	A-⊙
56	R243cc Cyclo- pentane	60.2 49.3	25 75	49	30 70	10-99 1-90	A-⊙
57	R244cb 2,2- dimethyl- butane	58 49.7	40 60	50	34 66	14-99 1-86	A-⊙
58	R235ca 2,2- dimethyl- butane	43.9 49.7	80 20	43	81 19	61-99 1-39	A-⊙
59	R244cb R122	58 71.9	80 20	58	75 25	55-95 5-45	A-⊙
60	R244cb R132b	58 46.8	30 70	45	29 71	9-49 51-91	A-⊙
61	R235ca R123	43.9 27.1	20 80	28	14 86	1-34 66-99	A-⊙
62	R235ca R132b	43.9 46.8	20 80	39	57 43	37-77 23-63	A-⊙

Table 1 (continued)

Exam- ples	Mixtures	B.P. (°C)	Charged composi- tion (wt%)	Boiling point of Azeo- trope (°C)	Azeo- tropic compo- sition (wt%)	Azeo- tropic- like compo- sition (wt%)	Test results
63	R235ca R141b	43.9 32	30 70	30	34 66	14-54 46-86	A-⊙
64	R243cc R122	60.2 71.9	80 20	60	77 23	57-97 3-43	A-⊙
65	R243cc R132b	60.2 46.8	20 80	46	24 76	4-44 56-96	A-⊙
66	R225ca R141	51.1 75.7	90 10	52	95 5	75-99 1-25	A-⊙
67	R225cb R141	56.1 75.7	90 10	56	89 11	69-99 1-31	A-⊙
68	R244cb R141	58 75.7	85 15	59	90 10	70-99 1-30	A-⊙
69	R225ca Methanol	51.1 64.5	97 3	46	94.6 5.4	75-99 1-25	A-⊙ B-⊙ C-⊙
70	R225cb Ethanol	56.1 78.3	97 3	53.8	95.6 4.4	74-99.5 0.5-26	A-⊙ B-⊙ C-⊙
71	R225cb Iso- propanol	56.1 82.4	97 3	54.9	97.9 2.1	77-99 1-23	A-⊙ B-⊙ C-⊙
72	R225cb Methanol	56.1 64.5	95 5	47.2	93.3 6.7	74-99 1-26	A-⊙ B-⊙ C-⊙
73	R225ca R225cb Ethanol	51.1 56.1 78.3	90 5 5	50	94.8 2.7 2.5	14-98 1-85 1-16	A-⊙ B-⊙ C-⊙

Table 1 (continued)

Exam- ples	Mixtures	B.P. (°C)	Charged composi- tion (wt%)	Boiling point of Azeo- trope (°C)	Azeo- tropic compo- sition (wt%)	Azeo- tropic- like compo- sition (wt%)	Test results
74	R225ca R225cb Methanol	51.1 56.1 64.7	89 6 5	46	89.8 5.6 4.6	14-98 1-85 1-16	A-⊙ B-⊙ C-⊙
75	R225ca Ethanol	51.1 78.3	98.5 1.5	50	97.3 2.7	75-99.5 0.5-25	A-⊙ B-⊙ C-⊙
76	R225ca Iso- propanol	51.1 82.4	-	-	-	76-99 1-24	A-⊙ B-⊙ C-⊙
77	R225ca R113 Dichloro- methane	51.1 47.6 39.8	35 15 50	-	38 15 47	15-61 8-44 34-70	A-⊙ B-⊙
78	R225cb R113 R132b	56.1 47.6 46.8	25 35 40	-	26 35 39	6-37 22-52 27-51	A-⊙
79	R225ca R113 R132b	51.1 47.6 46.8	35 25 40	-	32 29 39	22-55 10-46 21-55	A-⊙
80	R225cb R113 Dichloro- methane	56.1 47.6 39.8	25 25 50	-	26 24 50	8-38 8-47 34-63	A-⊙ B-⊙
81	R244ca R113 Dichloro- methane	54 47.6 39.8	25 20 55	-	25 19 56	6-33 9-41 43-68	A-⊙ B-⊙
82	R244ca R113 R132b	54 47.6 46.8	20 30 50	-	19 32 49	4-39 6-53 30-67	A-⊙

Table 1 (continued)

Exam- ples	Mixtures	B.P. (°C)	Charged composi- tion (wt%)	Boiling point of Azeo- trope (°C)	Azeo- tropic compo- sition (wt%)	Azeo- tropic- like compo- sition (wt%)	Test results
83	R225ca R113 trans- 1,2- dichloro- ethylene	51.1 47.6 47.7	40 20 40	-	41 22 37	28-52 7-39 25-48	A-⊙ B-⊙
84	R244ca R113 2-bromo- propane	54 47.6 59.4	30 60 10	-	25 62 13	8-36 48-85 3-28	A-⊙ B-⊙
85	R225ca R113 2-bromo- propane	51.1 47.6 59.4	40 50 10	-	42 47 11	29-60 11-61 3-29	A-⊙ B-⊙
86	R244ca R113 cis-1,2- dichloro- ethylene	54 47.6 60.6	20 60 20	-	22 58 20	4-38 40-77 9-32	A-⊙ B-⊙
87	R225ca R113 cis-1,2- dichloro- ethylene	56.1 47.6 60.6	35 50 15	-	32 53 15	19-43 39-60 8-22	A-⊙ B-⊙
88	R225ca R113 cis-1,2- dichloro- ethylene	51.1 47.6 60.6	40 45 15	-	42 45 13	25-54 38-58 8-22	A-⊙ B-⊙

Table 1 (continued)

Exam- ples	Mixtures	B.P. (°C)	Charged composi- tion (wt%)	Boiling point of Azeo- trope (°C)	Azeo- tropic compo- sition (wt%)	Azeo- tropic- like compo- sition (wt%)	Test results
89	R244ca	54	35	-	34	5-45	A-⊙
	R113	47.6	22		20	4-60	B-⊙
	trans- 1,2- dichloro- ethylene	47.7	48		46	26-59	
90	R225cb	56.1	35	-	36	27-51	A-⊙
	R113	47.6	25		27	6-44	B-⊙
	trans- 1,2- dichloro- ethylene	47.7	40		37	29-48	
91	R225cb	56.1	35	-	34	22-43	A-⊙
	R113	47.6	55		56	38-68	B-⊙
	2-bromo- propane	59.4	10		10	3-26	
92	R225cb	56.1	35	-	34	20-53	A-⊙
	R113	47.6	55		55	8-72	
	Cyclo- pentane	49.3	10		11	1-40	
93	R225ca	51.1	40	-	41	28-65	A-⊙
	R113	47.6	50		52	13-68	
	Cyclo- pentane	49.3	10		7	2-35	
94	R244ca	54	25	-	23	17-46	A-⊙
	R113	47.6	70		71	8-77	
	2,2- dimethyl- butane	49.7	5		6	2-56	

Table 1 (continued)

Exam- ples	Mixtures	B.P. (°C)	Charged composi- tion (wt%)	Boiling point of Azeo- trope (°C)	Azeo- tropic compo- sition (wt%)	Azeo- tropic- like compo- sition (wt%)	Test results
95	R225ca R113 1-chloro- propane	51.1 47.6 46.6	50 20 30	-	52 16 32	42-61 7-55 2-43	A-⊙ B-⊙
96	R225cb R113 1-chloro- propane	56.1 47.6 46.6	40 30 30	-	42 27 31	23-44 8-70 2-47	A-⊙ B-⊙
97	R244ca R113 2-chloro- 2-methyl- propane	54 47.6 50.7	20 60 20	-	22 57 21	4-33 41-78 8-31	A-⊙ B-⊙
98	R244ca R113 Cyclo- pentane	54 47.6 49.3	30 50 20	-	27 50 23	5-45 9-74 12-46	A-⊙
99	R225ca R113 2-chloro- 2-methyl- propane	51.1 47.6 50.7	45 50 5	-	40 55 5	28-56 12-64 2-32	A-⊙ B-⊙
100	R225cb R113 2-chloro- 2-methyl- propane	56.1 47.6 50.7	30 60 10	-	31 58 11	17-38 41-75 2-21	A-⊙ B-⊙
101	R224ca R113 1-chloro- propane	54 47.6 46.6	35 20 45	-	36 19 45	9-39 9-84 2-60	A-⊙ B-⊙

Table 1 (continued)

Exam- ples	Mixtures	B.P. (°C)	Charged composi- tion (wt%)	Boiling point of Azeo- trope (°C)	Azeo- tropic compo- sition (wt%)	Azeo- tropic- like compo- sition (wt%)	Test results
102	R225ca R225cb 2-methyl- pentane	51.1 56.1 60.3	90 5 5	-	90 7 3	36-97 1-51 1-16	A-⊙
103	R225ca R225cb 2,3- dimethyl- butane	51.1 56.1 58.0	85 10 5	-	88 8 4	6-94 1-83 1-26	A-⊙
104	R225ca R225cb 2-chloro- 2-methyl- propane	51.1 56.1 50.7	50 10 40	-	50 12 38	6-67 4-67 1-58	A-⊙ B-⊙
105	R225ca R225cb 1-chloro- propane	51.1 56.1 46.6	40 15 45	-	41 14 45	7-56 7-61 1-54	A-⊙ B-⊙
106	R225ca R225cb 2-bromo- propane	51.1 56.1 59.4	55 10 35	-	54 10 36	6-66 5-64 10-48	A-⊙ B-⊙
107	R225ca R225cb cis-1,2- dichloro- ethylene	51.1 56.1 60.6	60 10 30	-	58 12 30	6-70 4-74 10-38	A-⊙ B-⊙

Table 1 (continued)

Exam- ples	Mixtures	B.P. (°C)	Charged composi- tion (wt%)	Boiling point of Azeo- trope (°C)	Azeo- tropic compo- sition (wt%)	Azeo- tropic- like compo- sition (wt%)	Test results
108	R225ca	51.1	40	-	42	8-57	A-⊙
	R225cb	56.1	15		13	6-54	B-⊙
	trans- 1,2- dichloro- ethylene	47.7	45		45	10-59	
109	R225ca	51.1	80	-	80	40-89	A-⊙
	R225cb	56.1	10		8	2-37	B-⊙
	R122	71.9	10		12	3-23	
110	R225ca	51.1	80	-	84	44-92	A-⊙
	R225cb	56.1	10		8	2-41	B-⊙
	R141	75.7	10		8	1-17	
111	R225ca	51.1	35	-	36	6-44	A-⊙
	R225cb	56.1	10		11	4-44	B-⊙
	R132b	46.8	55		53	44-73	
112	R225ca	56.1	25	-	20	8-31	A-⊙
	R141b	32	65		67	36-88	B-⊙
	Dichloro- methane	39.8	10		13	3-38	
113	R225ca	51.1	30	-	26	8-41	A-⊙
	R141b	32	60		62	32-84	B-⊙
	Dichloro- methane	39.8	10		12	3-31	
114	R225ca	51.1	15	-	12	6-33	A-⊙
	R141b	32	5		7	2-33	B-⊙
	R123	27.1	80		81	44-86	
115	R225ca	51.1	30	-	33	5-47	A-⊙
	R225cb	56.1	10		9	3-42	
	R113	47.6	60		58	5-79	

Table 1 (continued)

Exam- ples	Mixtures	B.P. (°C)	Charged composi- tion (wt%)	Boiling point of Azeo- trope (°C)	Azeo- tropic compo- sition (wt%)	Azeo- tropic- like compo- sition (wt%)	Test results
116	R225ca	51.1	25	-	25	9-49	A-⊙
	R225cb	56.1	21		21	8-39	B-⊙
	Dichloro- methane	39.8	55		54	5-70	
117	R244ca	54	15	-	16	6-31	A-⊙
	R141b	32	70		68	38-90	B-⊙
	Dichloro- methane	39.8	15		16	3-40	
118	R244ca	54	20	-	21	5-58	A-⊙
	R225cb	56.1	40		42	7-66	B-⊙
	2-bromo- propane	59.4	40		37	5-54	
119	R244ca	54	30	-	31	4-58	A-⊙
	R225cb	56.1	40		35	7-71	B-⊙
	cis-1,2- dichloro- ethylene	60.6	30		34	4-43	
120	R244ca	54	15	-	15	8-58	A-⊙
	R225cb	56.1	40		39	9-65	B-⊙
	1-chloro- propane	46.6	45		46	5-71	
121	R244ca	54	20	-	22	7-55	A-⊙
	R225cb	56.1	30		32	8-56	B-⊙
	2-chloro- 2-methyl- propane	50.7	50		46	5-74	
122	R244ca	54	60	-	62	29-87	A-⊙
	R225cb	56.1	20		20	6-68	
	2,3- dimethyl- butane	58	20		18	2-29	

Table 1 (continued)

Exam- ples	Mixtures	B.P. (°C)	Charged composi- tion (wt%)	Boiling point of Azeo- trope (°C)	Azeo- tropic compo- sition (wt%)	Azeo- tropic- like compo- sition (wt%)	Test results
123	R244ca R225cb R132b	54 56.1 46.8	20 20 60	-	18 24 58	5-42 7-50 41-80	A-⊙ B-⊙
124	R244ca R225cb trans- 1,2- dichloro- ethylene	54 56.1 47.7	30 25 45	-	30 26 44	5-55 8-57 5-61	A-⊙ B-⊙
125	R244ca R225cb Cyclo- pentane	54 56.1 49.3	25 30 45	-	25 32 45	8-56 9-55 5-69	A-⊙
126	R244ca R225cb Dichloro- methane	54 56.1 39.8	20 20 60	-	17 24 59	7-35 9-42 45-73	A-⊙ B-⊙
127	R244ca R225ca 2,2- dimethyl- butane	54 51.1 49.7	40 20 40	-	39 19 42	7-61 8-71 5-72	A-⊙
128	R244ca R225ca Dichloro- methane	54 51.1 39.8	10 30 60	-	12 34 54	5-41 9-48 40-73	A-⊙ B-⊙
129	R244ca R225ca R132b	54 51.1 46.8	10 40 50	-	9 40 51	2-37 7-50 35-72	A-⊙ B-⊙

Table 1 (continued)

Exam- ples	Mixtures	B.P. (°C)	Charged composi- tion (wt%)	Boiling point of Azeo- trope (°C)	Azeo- tropic compo- sition (wt%)	Azeo- tropic- like compo- sition (wt%)	Test results
130	R244ca R225ca R141	54 51.1 75.7	25 70 5	-	24 70 6	3-49 47-95 0.1-17	A-⊙ B-⊙
131	R244ca R225ca Cyclo- pentane	54 51.1 49.3	10 55 35	-	11 55 34	5-55 9-67 3-53	A-⊙
132	R244ca R225ca R122	54 51.1 71.9	20 70 10	-	21 70 9	3-59 36-93 1-22	A-⊙ B-⊙
133	R244ca R225ca trans- 1,2- dichloro- ethylene	54 51.1 47.7	10 50 40	-	11 47 42	3-69 8-78 3-54	A-⊙ B-⊙
134	R244ca R225ca cis-1,2- dichloro- ethylene	54 51.1 60.6	8 62 30	-	10 60 30	3-59 7-75 3-38	A-⊙ B-⊙
135	R244ca R225ca 2-bromo- propane	54 51.1 59.4	10 60 30	-	8 58 34	3-58 6-71 3-44	A-⊙ B-⊙
136	R244ca R225cb R141	54 56.1 75.7	45 45 10	-	47 47 6	22-86 6-72 1-21	A-⊙ B-⊙

Table 1 (continued)

Exam- ples	Mixtures	B.P. (°C)	Charged composi- tion (wt%)	Boiling point of Azeo- trope (°C)	Azeo- tropic compo- sition (wt%)	Azeo- tropic- like compo- sition (wt%)	Test results
137	R225ca R225cb Cyclo- pentane	51.1 56.1 49.3	50 10 40	-	48 15 37	10-88 8-70 3-58	A-⊙
138	R244ca R225cb R122	54 56.1 71.9	50 40 10	-	45 45 10	8-83 6-84 3-28	A-⊙ B-⊙
139	R244ca R225ca 2,3- dimethyl- butane	54 51.1 58	30 65 5	-	29 67 4	3-84 13-94 0.1-19	A-⊙
140	R244ca R225ca 1-chloro- propane	54 51.1 46.6	10 50 40	-	11 48 41	3-48 7-62 3-56	A-⊙ B-⊙
141	R244ca R225ca 2-chloro- 2-methyl- propane	54 51.1 50.7	10 60 30	-	10 54 36	3-56 6-72 3-54	A-⊙ B-⊙
142	R244ca R225cb 2,2- dimethyl- butane	54 56.1 49.7	45 10 45	-	42 14 44	7-76 8-62 3-73	A-⊙

Table 1 (continued)

Exam- ples	Mixtures	B.P. (°C)	Charged composi- tion (wt%)	Boiling point of Azeo- trope (°C)	Azeo- tropic compo- sition (wt%)	Azeo- tropic- like compo- sition (wt%)	Test results
143	R244ca Methanol	54 64.7	-	-	-	76-99 1-24	A-⊙ B-⊙
144	R244ca Ethanol	54 78.3	-	-	-	77-99 1-23	A-⊙ B-⊙
145	R244ca Iso- propanol	54 82.4	-	-	-	79-99 1-21	A-⊙ B-⊙
146	R225ca R244ca Ethanol	51.1 54 78.3	-	-	-	50-80 10-40 1-10	A-⊙ B-⊙
147	R225cb R224ca Ethanol	56.1 54 78.3	-	-	-	40-80 10-50 1-10	A-⊙ B-⊙
148	R225ca R225cb R244ca Ethanol	51.1 56.1 54 78.3	-	-	-	5-99 3-99 1-69 1-35	A-⊙ B-⊙
149	R225ca R244ca Methanol	51.1 54 64.7	-	-	-	50-80 10-40 1-10	A-⊙ B-⊙
150	R225cb R244ca Methanol	56.1 54 64.7	-	-	-	40-80 10-50 1-10	A-⊙ B-⊙
151	R225ca R225cb R244ca Methanol	51.1 56.1 54 64.7	-	-	-	5-99 3-99 1-69 1-35	A-⊙ B-⊙

Table 1 (continued)

Examp- ples	Mixtures	B.P. (°C)	Charged composi- tion (wt%)	Boiling point of Azeo- trope (°C)	Azeo- tropic compo- sition (wt%)	Azeo- tropic- like compo- sition (wt%)	Test results
152	R225ca R225cb Iso- propanol	51.1 56.1 82.4	-	-	-	1-98 1-98 1-16	A-⊙ B-⊙

20 REFERENCE EXAMPLES

For the purpose of ascertaining the effects of the azeotropic-like mixture of the present invention for stabilization, the following test was applied to the mixture as identified in Table 2.

In accordance with JIS K1600, a metal test piece was placed in both the liquid phase portion and the gas phase portion of the stabilized mixture as identified in Table 2, and after 48 hours, the state of corrosion of the test piece was inspected. The results are shown in Table 2.

Azeotropic-like mixture

AA: R225ca/R225cb/methanol = 47 wt%/47 wt%/6 wt%

Stabilizer

30 NM: Nitromethane

DIPA: Diisopropylamine

Am: β -Amylene

TPH: Triphenylphosphite

DME: 1,2-Dimethoxyethane

35 s-Bu: sec-Butanol

ECH: Epichlorohydrin

BHT: 2,6-Di-t-butyl-o-cresol

BTA: 1,2,3-Benzotriazole

PH: Phenol

40 DO: 1,4-Dioxane

MeA: Methyl acetate

BO: 1,2-Buthyleneoxide

MP: N-methylpyrrole

MIBK: Methyl isobutyl ketone

45 i-Bu: Isobutanol

Appearance of test piece

⊙: No corrosion

O: No substantial corrosion

Δ: Corrosion slightly observed

50 X: Substantial corrosion observed.

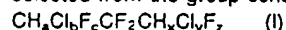
Table 2

Reference Examples	Stabilized mixture (wt%)	Corrosion of test piece		
		Fe	Cu	Ag
AA01	AA(99.5)/PH(0.5)	⊙	○	○
AA02	AA(99.5)/DIPA(0.5)	⊙	○	○
AA03	AA(99.5)/Am(0.5)	⊙	○	○
AA04	AA(99.5)/TPH(0.5)	⊙	○	○
AA05	AA(99.5)/MP(0.5)	⊙	○	○
AA06	AA(99.5)/BTA(0.5)	○	⊙	○
AA07	AA(99)/NM(1)	⊙	○	○
AA08	AA(99)/DO(1)	⊙	○	○
AA09	AA(99)/MeA(1)	⊙	○	○
AA10	AA(99)/BO(1)	⊙	○	○
AA11	AA(99)/DME(1)	⊙	○	○
AA12	AA(99)/s-Bu(1)	⊙	○	○
AA13	AA(99)/MIBK(1)	⊙	○	○
AA14	AA(99)/ECH(1)	⊙	○	○
AA15	AA(98.5)/NM(1)/BTA(0.5)	⊙	⊙	⊙
AA16	AA(97.5)/NM(1)/BO(1)/BHT(0.5)	⊙	⊙	○
AA17	AA(97)/NM(1)/BO(1)/BHT(0.5)/BTA(0.5)	⊙	⊙	⊙
AA18	AA(96)/NM(1)/BTA(0.5)/BO(1)/i-Bu(1)/BHT(0.5)	⊙	⊙	⊙
Comparative Example	AA(100)	⊙	Δ	Δ

The hydrochlorofluorocarbon azeotropic or azeotropic-like mixture of the present invention is non-flammable or hardly flammable and has excellent properties equal or superior to conventional CFCs. Further, the mixture shows no substantial change in the composition during boiling and evaporating, since it has an azeotropic composition or an azeotropic-like composition, and it can be used in the same manner as a conventional single CFC and thus has a merit that it requires no substantial change of the conventional technique. Further, it is excellent in the properties for dissolving and removing a flux or oil like R113 which is commonly used as a solvent, and thus it is useful as a cleaning agent which may be an alternative for R113.

Claims

1. A hydrochlorofluorocarbon azeotropic or azeotropic-like mixture comprising at least one member selected from the group consisting of hydrochlorofluoropropanes of the formula I:



wherein $a+b+c=3$, $x+y+z=3$, $a+x \geq 1$, $b+y \geq 1$, and $0 \leq a, b, c, x, y, z \leq 3$, and at least one member selected from the group of compounds II consisting of halogenated hydrocarbons having a boiling point of from 20 to 85°C other than said hydrochlorofluoropropanes, hydrocarbons having a boiling point of from 20 to 85°C and alcohols having from 1 to 4 carbon atoms.

2. The mixture according to Claim 1, wherein the hydrochlorofluoropropanes of the formula I are 3,3-dichloro-1,1,1,2,2-pentafluoropropane (R225ca), 1,3-dichloro-1,1,2,2,3-pentafluoropropane (R225cb), 3-chloro

1,1,2,2-tetrafluoropropane (R244ca), 1-chloro-1,2,2,3-tetrafluoropropane (R244cb), 3-chloro-1,1,2,2,3-pentafluoropropane (R235ca) and 1,1-dichloro-1,2,2-trifluoropropane (R243cc).

3. The mixture according to Claim 1, wherein the halogenated hydrocarbons having a boiling point of from 20 to 85 °C other than said hydrochlorofluoropropanes are chlorinated hydrocarbons, fluorinated hydrocarbons and brominated hydrocarbons having from 1 to 4 carbon atoms.

4. The mixture according to Claim 1, wherein the hydrocarbons having a boiling point of from 20 to 85 °C have from 5 to 8 carbon atoms.

5. The mixture according to Claim 1, wherein the alcohols having from 1 to 4 carbon atoms are methanol, ethanol and isopropanol.

6. The mixture according to Claim 3, wherein the chlorinated hydrocarbons having from 1 to 4 carbon atoms are dichloromethane, trans-1,2-dichloroethylene, cis-1,2-dichloroethylene, 1-chloropropane and 2-chloro-2-methylpropane.

7. The mixture according to Claim 3, wherein the fluorinated hydrocarbons are 1,1,2-trichlorotrifluoroethane (R113), 1,1,2-trichloro-2,2-difluoroethane (R122), 1,1-dichloro-2,2,2-trifluoroethane (R123), 1,2-dichloro-1,1-difluoroethane (R132b), 1,2-dichloro-1 fluoroethane (R141) and 1,1-dichloro-1-fluoroethane (R141b).

8. The mixture according to Claim 3, wherein the brominated hydrocarbon is 2-bromopropane.

9. The mixture according to Claim 4, wherein the hydrocarbons having from 5 to 8 carbon atoms are cyclopentane, 2,2-dimethylbutane, 2-methylpentane and 2,3-dimethylbutane.

10. The mixture according to Claim 1, which comprises R225ca and at least one member selected from the group consisting of R141, R141b, R141b/dichloromethane, R141b/R123, dichloromethane, R122, R132b, R113, R113/R132b, R113/dichloromethane, R113/2-bromopropane, cyclopentane, 2,2-dimethylbutane, 2-methylpentane, 2-bromopropane, 2,3-dimethylbutane, trans-1,2-dichloroethylene, cis-1,2-dichloroethylene, R113/cyclopentane, R113/1-chloropropane, R113/trans-1,2-dichloroethylene, R113/cis-1,2-dichloroethylene, R113/2-chloro-2-methylpropane, methanol, ethanol and isopropanol.

11. The mixture according to Claim 1, which comprises R225cb and at least one member selected from the group consisting of R141, R141b, R141b/dichloromethane, dichloromethane, R122, R132b, R113, R113/R132b, R113/dichloromethane, cyclopentane, 2,2-dimethylbutane, 2-methylpentane, trans-1,2-dichloroethylene, cis-1,2-dichloroethylene, 2,3-dimethylbutane, 2-bromopropane, R113/cyclopentane, R113/1-chloropropane, R113/trans-1,2-dichloroethylene, R113/cis-1,2-dichloroethylene, R113/2-bromopropane, R113/2-chloro-2-methylpropane, methanol, ethanol and isopropanol.

12. The mixture according to Claim 1, which comprises R224ca and at least one member selected from the group consisting of R141b, R141b/dichloromethane, dichloromethane, R122, R132b, R113, R113/R132b, R113/dichloromethane, cyclopentane, 2,2-dimethylbutane, 2-bromopropane, 2-methylpentane, 2,3-dimethylbutane, R113/2 bromopropane, R113/cyclopentane, R113/2,2-dimethylbutane, R113/1-chloropropane, R113/trans-1,2-dichloroethylene, R113/cis-1,2-dichloroethylene, R113/2-chloro-2-methylpropane, trans-1,2-dichloroethylene, cis-1,2-dichloroethylene, methanol, ethanol and isopropanol.

13. The mixture according to Claim 1, which comprises R225ca, R225cb and at least one member selected from the group consisting of 2-methylpentane, 2,3-dimethylbutane, 2-chloro-2-methylpropane, 1-chloropropane, 2-bromopropane, cis-1,2-dichloroethylene, trans-1,2-dichloroethylene, cyclopentane, R122, R141, R132b, R113, dichloromethane, methanol, ethanol and isopropanol.

14. The mixture according to Claim 1, which comprises R225cb, R244ca and at least one member selected from the group consisting of 2,2-dimethylbutane, cyclopentane, 2,3-dimethylbutane, cis-1,2-dichloroethylene, 2-bromopropane, 1-chloropropane, 2-chloro-2-methylpropane, R132b, trans-1,2-dichloroethylene, dichloromethane, R141, R122, methanol and ethanol.

15. The mixture according to Claim 1, which comprises R225ca, R244ca and at least one member selected from the group consisting of 2,2-dimethylbutane, cyclopentane, 2,3-dimethylbutane, dichloromethane, R132b, R141, R122, trans-1,2-dichloroethylene, cis-1,2-dichloroethylene, 2-bromopropane, 1-chloropropane, 2-chloro-2-methylpropane, methanol and ethanol.

16. The mixture according to Claim 1, which comprises R235ca and at least one member selected from the group consisting of trans-1,2-dichloroethylene, cis-1,2-dichloroethylene, dichloromethane, cyclopentane, 2-bromopropane, 2,2-dimethylbutane, R113, R123, R132b and R141b.

17. The mixture according to Claim 1, which comprises R243cc and at least one member selected from the group consisting of trans-1,2-dichloroethylene, cis-1,2-dichloroethylene, 2-bromopropane, 2-methylpentane, dichloromethane, cyclopentane, 2,3-dimethylbutane, R122 and R132b.

18. The mixture according to Claim 1, which comprises R244cb and at least one member selected from the group consisting of dichloromethane, cyclopentane, 2,2-methylbutane, 2,3-dimethylbutane, 2-methylpentane, 2-bromopropane, R122, R132b, R113, trans-1,2-dichloroethylene, cis-1,2-dichloroethylene and R141.

19. The mixture according to Claim 1, which comprises R225ca, R225cb, R244ca and methanol.
20. The mixture according to Claim 1, which comprises R225ca, R225cb, R244ca and ethanol.

5

10

15

20

25

30

35

40

45

50

55



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number ✓

EP 90 10 2015

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
P,A	EP-A-0 347 924 (ASAHI GLASS CO., LTD) * Claims 1,2; page 3, lines 19-53; page 4, lines 16-21 *	1-7	C 11 D 7/50 C 23 G 5/028 C 07 C 19/08
A	US-A-3 936 387 (R.E. REUSER) * Claim 1 *	1,5	
A	US-A-3 080 430 (W.V. COHEN) * Claims 1,2; column 2, lines 8-13 *	1,2	
A	FR-A-2 128 555 (IMPERIAL CHEMICAL INDUSTRIES)		
A	US-A-3 476 819 (F.D. TRISHLER)		
A	PATENT ABSTRACTS OF JAPAN, vol. 13, no. 124 (C-580)[3472], 27th March 1989; & JP-A-63 295 699 (DAIKIN LTD) 02-12-1988		
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 11 D 7/00 C 23 G 5/00 C 07 C 19/00
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 18-04-1990	Examiner TORFS F.M.G.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

EPO FORM 1503 (01.87) (P0001)